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SUPEROLEOPHOBIC SURFACE FORMATION ON FLUOROPOLYMER / NANOCOMPOSITE SURFACES

15 October 2014

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Outline

- Fluoropolymer / Fluorinated Silica Nanocomposites
  - Less Binder -> More Roughness -> Superoleophobicity
- Effect of Fluoropolymer Type
- Effect of Silica Particle Type
  - Fumed vs. Precipitated
  - Fluorinated vs. Non-fluorinated

Acknowledgements: Air Force Research Laboratory, Air Force Office of Scientific Research (AFOSR) – program support; PWG Team Members!

Baseline fluoropolymer Nanocomposite

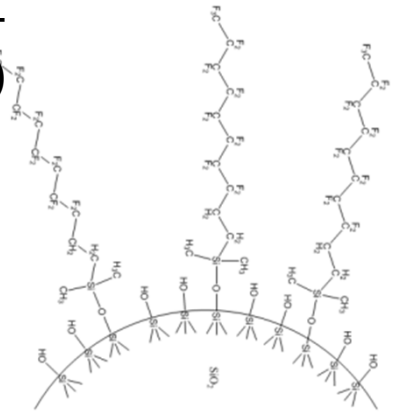
- Hi-Sil233 (PPG Industries):
  - -precipitated amorphous silica
  - -Surface area, BET: 135 m^2/g
  - -Silanol group density: 5-12 nm^{-2}
  - -Average particle size: 22 nm

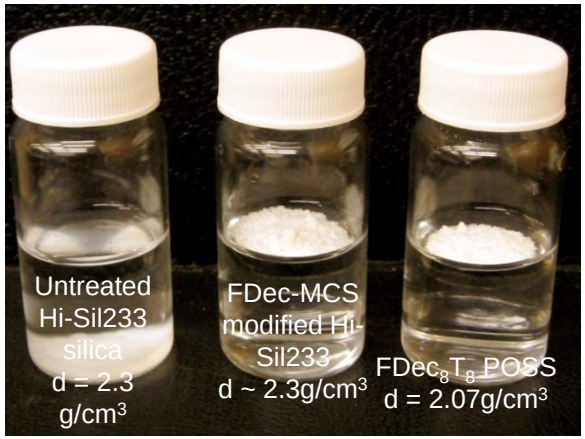
5 mg/mL fluoropolymer in AK225G

Viton® Extreme ETP-600S: DuPont terpolymer consisting of ethylene, tetrafluoroethylene, perfluoro(methylvinyl) ether, and bromotetrafluorobutene

Properties of 1H,1H,2H,2H-heptadecafluorodecyl(dimethyl)chloro-silane-treated Hi-Sil233 (FF-Hi-Sil233)

Average Diameter (nm)	22
BET Surface Area (m^2/g)	92
BET C Constant	21
Water Vapor Uptake (wt%)	2.8
Wt % Fluorine	9.9
Grafting Density (chains nm^{-2})	1.6
Graft Layer Molar Volume (cc)	311
Average Thickness of Graft (nm)	0.8





Campos, R.; Guenthner, A. J.; Haddad, T. S.; Mabry, J. M. "Fluoroalkyl-functionalized Silica Particles: Synthesis, Characterization, and Wetting Characteristics", *Langmuir*, 27,10206-10215 (2011).

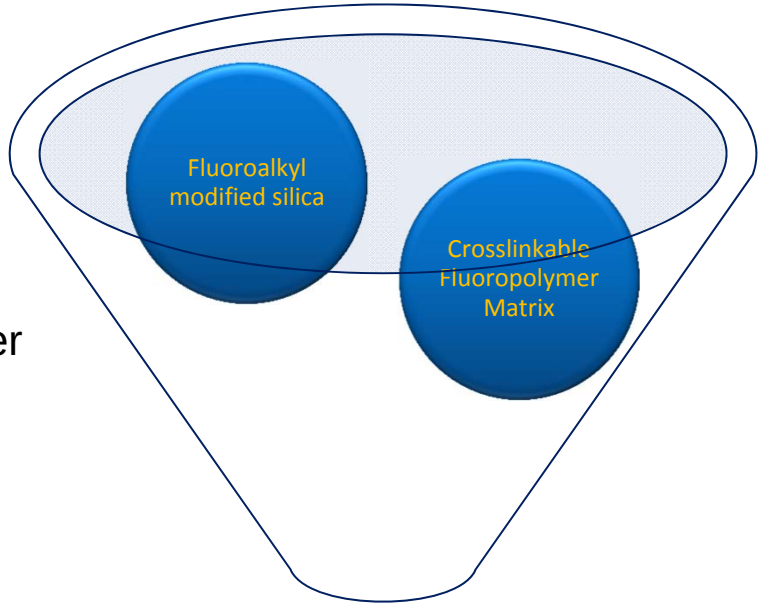
Campos, R.; Guenthner, A. J.; Meuler, A. J.; Tuteja, A.; Cohen, R. E.; McKinley, G. H.; Haddad, T. S.; Mabry J. M. "Superoleophobic surfaces through control of stochastic sprayed-on topography", *Langmuir*, 28, 9834-9841 (2012).

Spray Coating Process

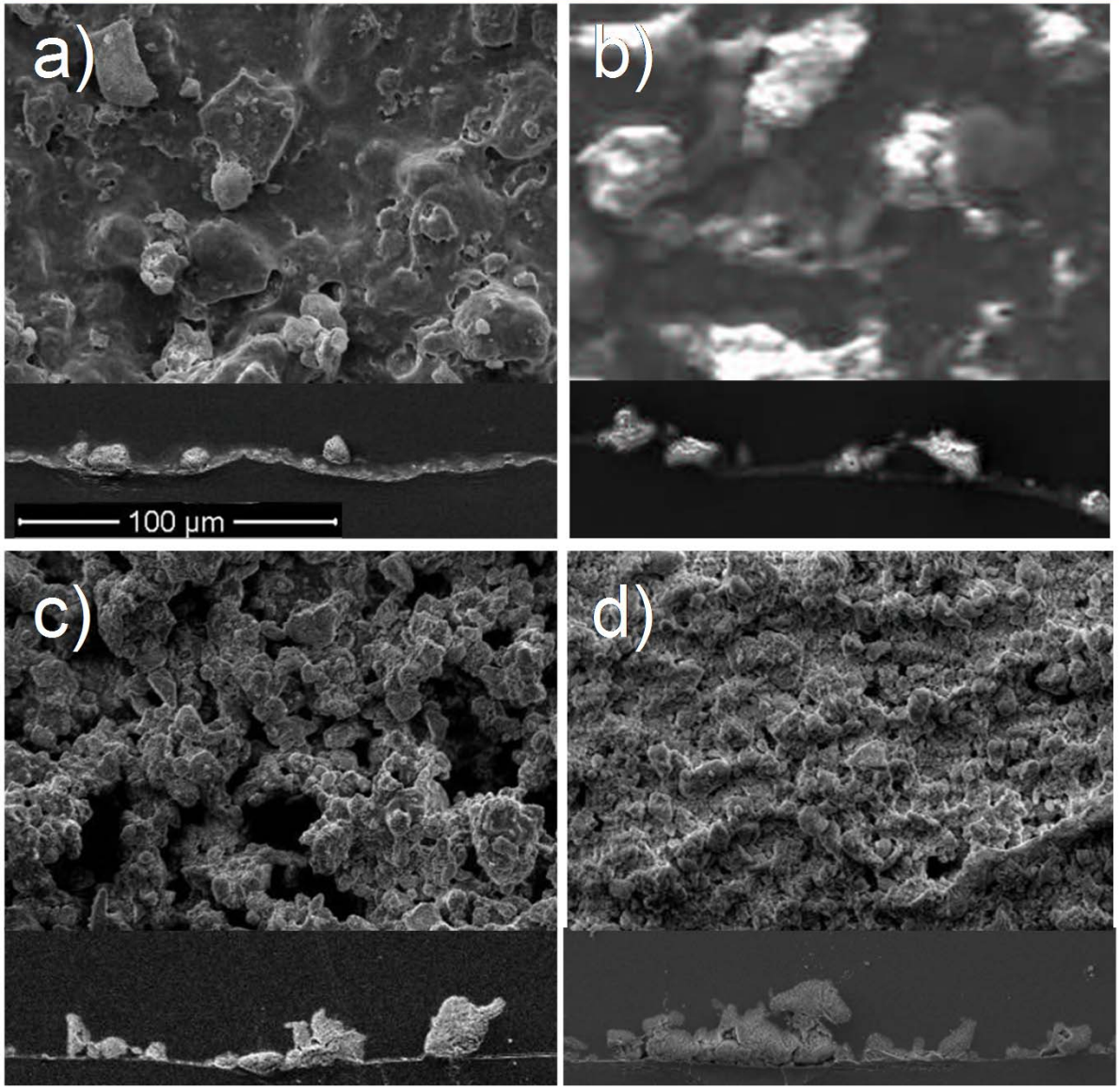
- Silica Types
  - FF-Modified Hi-Sil233
  - Unmodified Hi-Sil233
  - FF-Modified 7 nm fumed silica, 390 m^2/g, Aldrich)

- fluoropolymer Types
  - Viton Extreme ETP-600S (described previously)
  - Technoflon BR 9151: Solvay Solexis pentapolymer consisting of Vinylidene (VF_2), HFP (hexafluoropropylene), TFE (tetrafluoroethylene), PMVE (perfluoromethylvinylether CF_2=CF-OCF_3) and ethylene

- Spray coating done via airbrush (Paasche, VLSTPRO) with a 1.06 mm diameter tip using compressed air (25 psi). The airbrush was repeatedly passed over the substrate laterally at an approximate distance of 15-20 cm from the substrate until 20 mL of the coating mixture had been deposited. The resultant deposition level is around is 20 mg/cm^2.



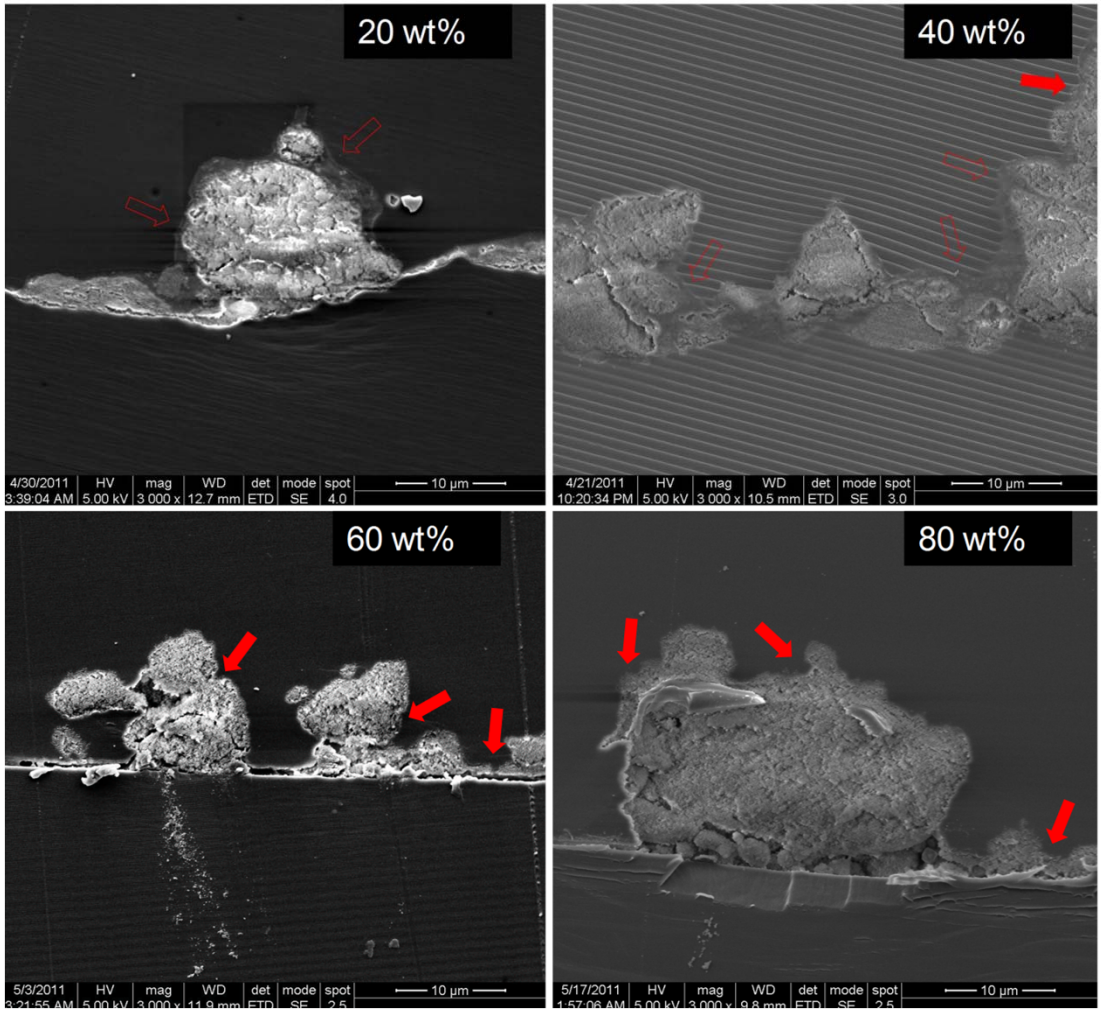
Coating Morphology



Top-down (upper panels) and cross-sectional (lower panels) views of FF-Hi-Sil233 / Viton coatings with silica to fluoro-polymer ratios of:
a) 20:80 (wt) b) 40:60 (wt)
c) 60:40 (wt) d) 80:20 (wt)

At low loadings, “islands” of FF-silica float in a “sea” of fluoropolymer. At higher loadings, the FF-silica forms larger and larger aggregates, with little or no fluoropolymer between aggregates

Effect of Binder on Sub-Micron Roughness

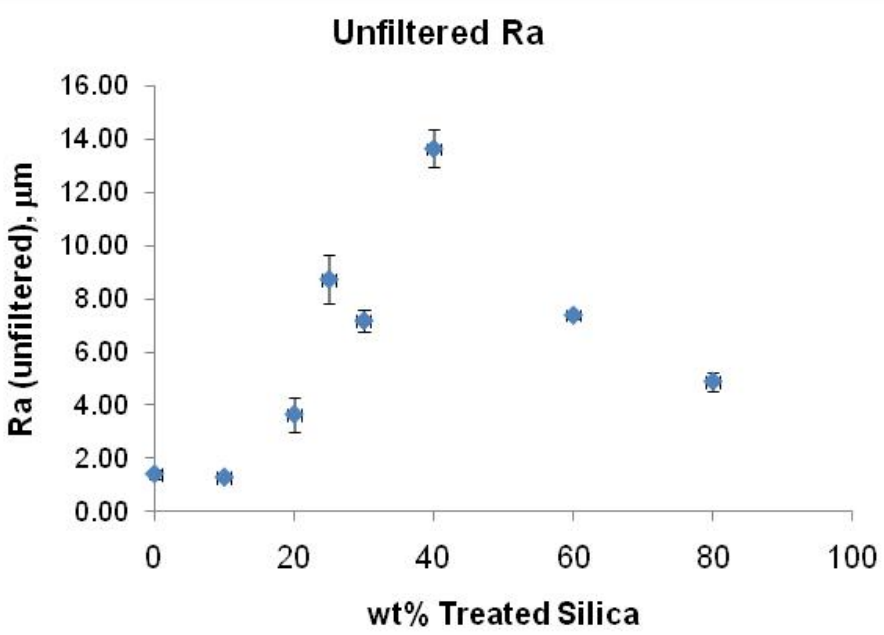


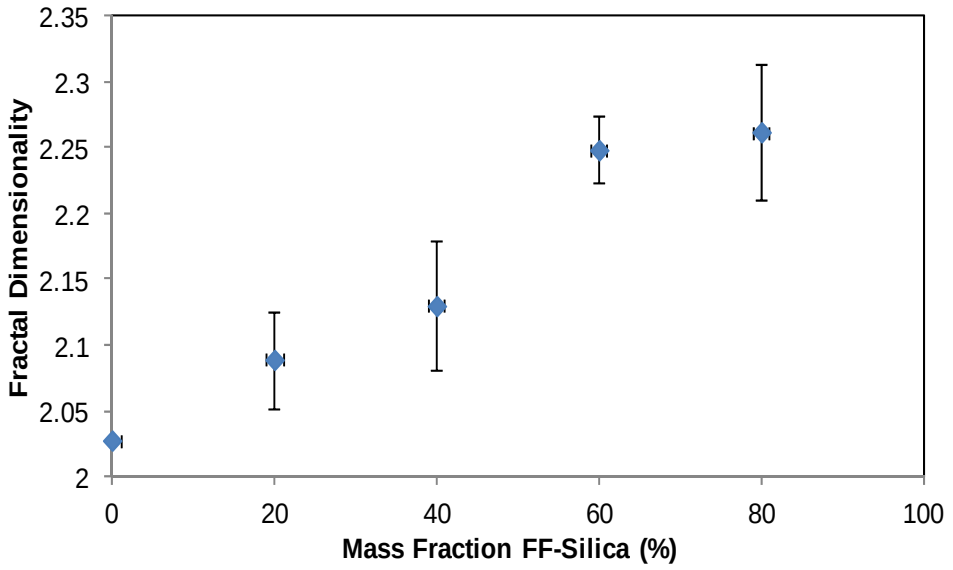
Cross-sectional morphology of FF-Hi-Sil233 / Viton coatings at the FF-silica loading levels indicated. Unfilled arrows indicate fine features in the silica particle that are filled in by binder; filled arrows indicate where such features are conformal to the surface.

The fluoropolymer binder "fills in" fine features in the coating surface that would otherwise be present

Quantification of Nanocomposite Roughness Characteristics

FF-Hi-Sil233 / Viton®



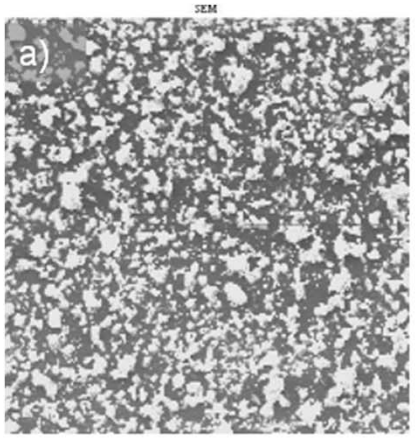


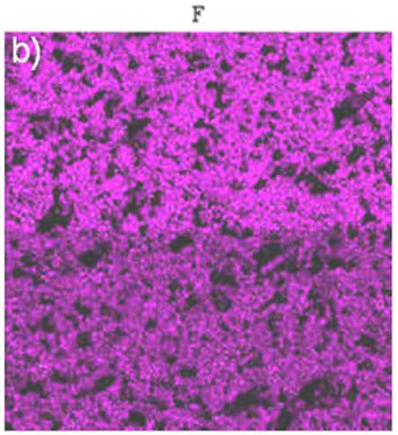
Average roughness as measured by interferometry, sensitive to features larger than about 1 µm

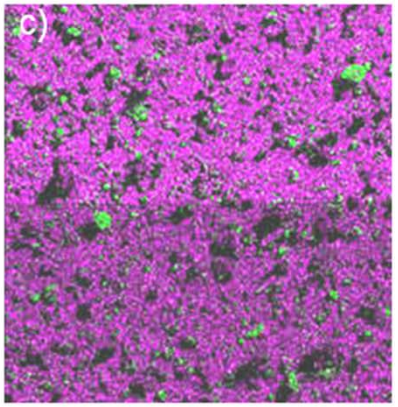
Fractal dimensionality as measured by cross-sectional SEM; sensitive to features from 0.1 - 10µm

At higher silica loading levels, the roughness exists principally at sub-micron length scales

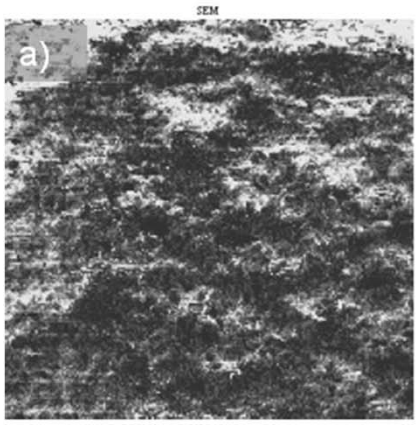
Elemental Composition of FF-Hi-Sil233 /Viton Surfaces

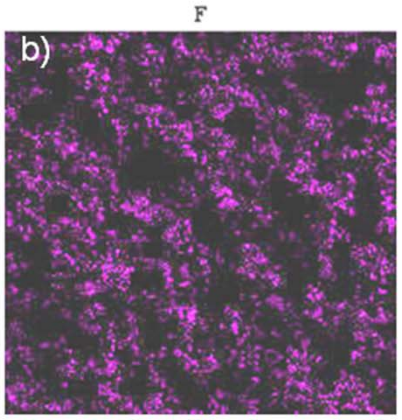


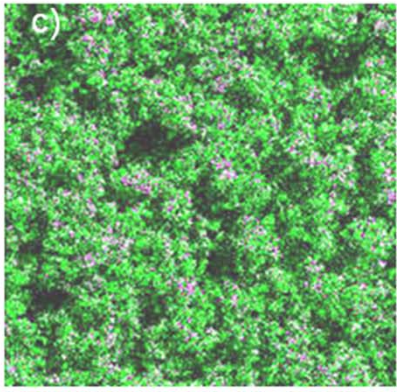




20 wt% FF-Hi-Sil233





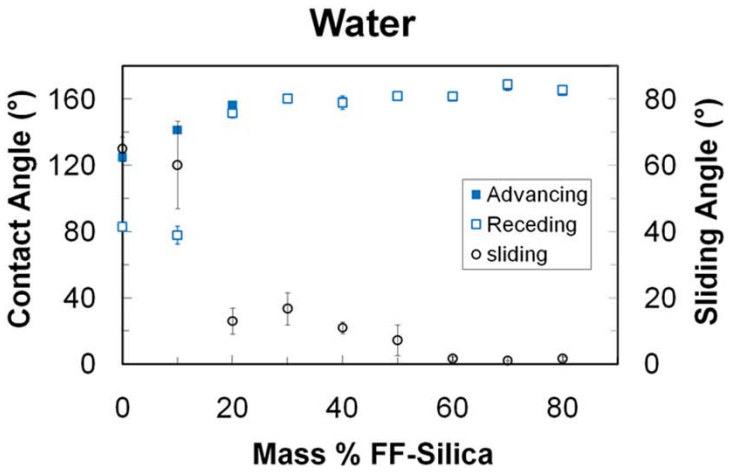


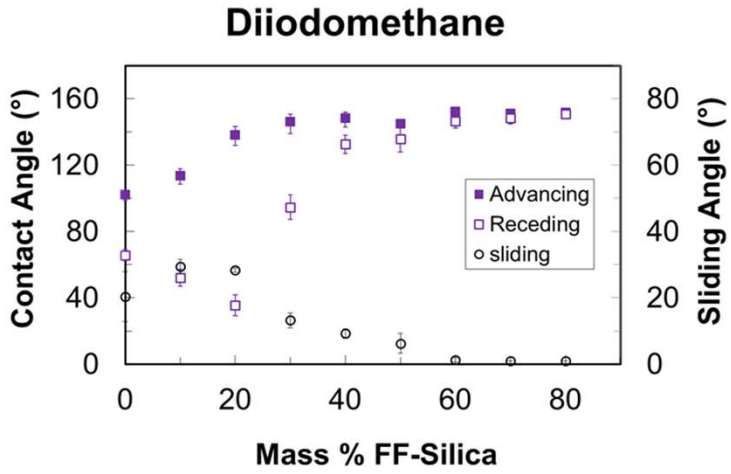
80 wt% FF-Hi-Sil233

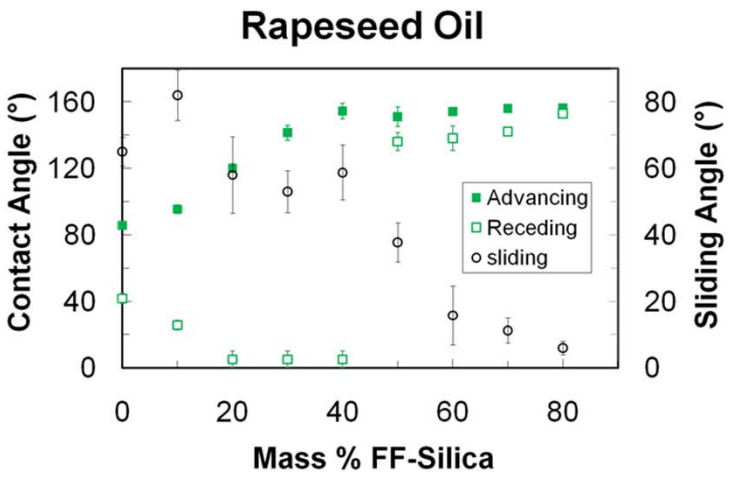
Pink = F; Green = Si

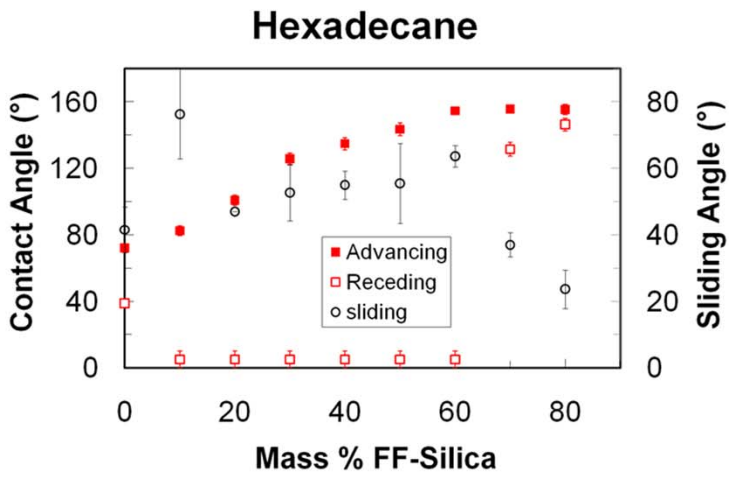
At 80 wt% loading, any binder pools on the surface are few and isolated

Superamphiphobicity of FF-Silica / Viton Surfaces



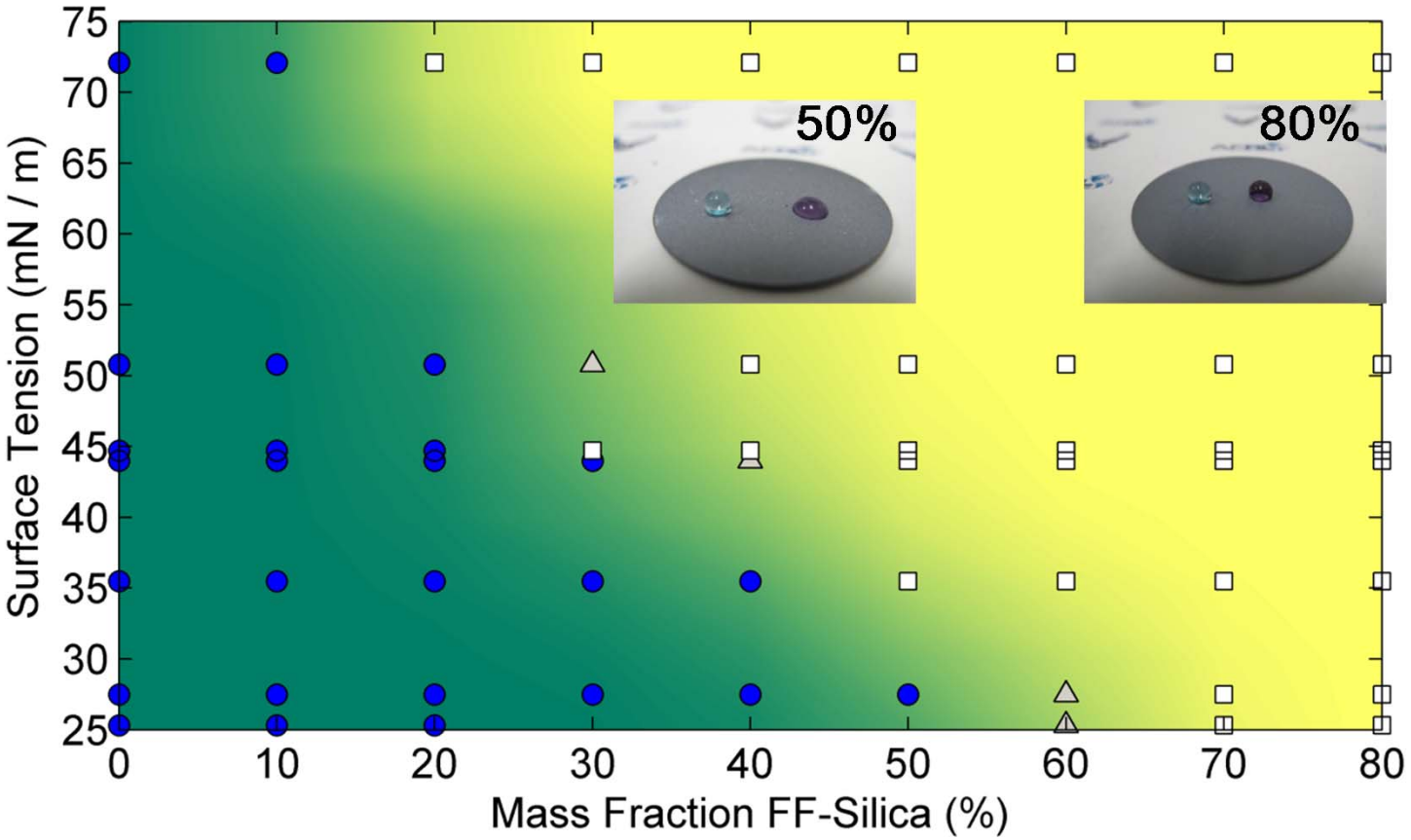






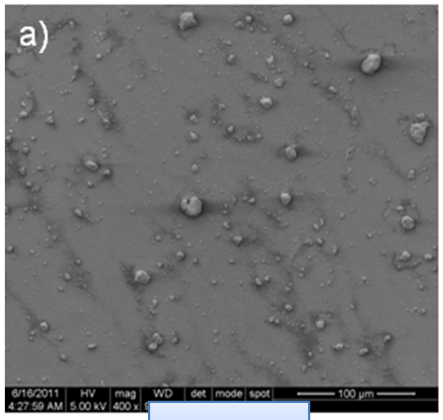
Liquid repulsion characteristics can be tuned by adjusting the level of FF-silica

Superamphiphobicity of FF-Silica / Viton Surfaces

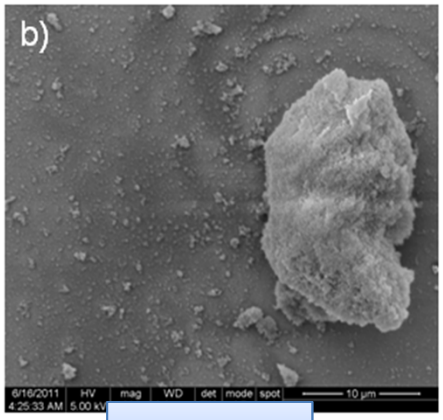


Parameter map showing liquid repulsion characteristics; filled symbols = fully wetted state; open symbols = Cassie-Baxter state; triangles = mixed behavior

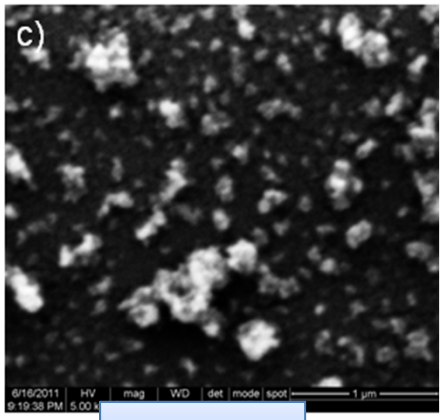
Effect of Silica Type on Silica Particle Morphology



400x

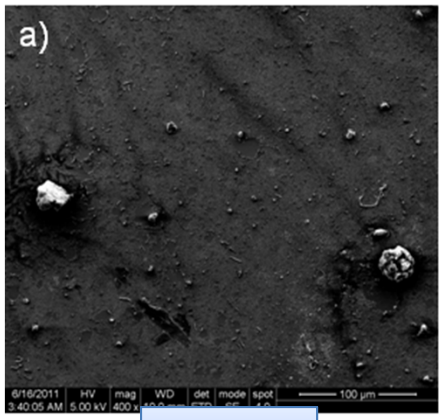


4000x



50000x

Hi-Sil233 Precipitated



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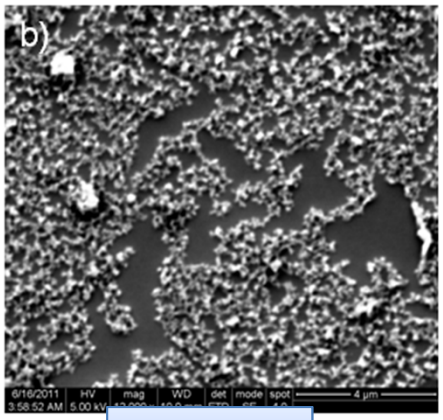
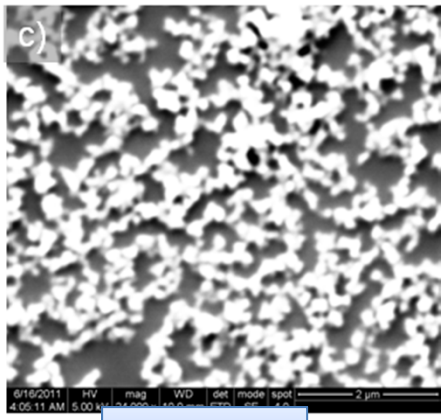


12000x

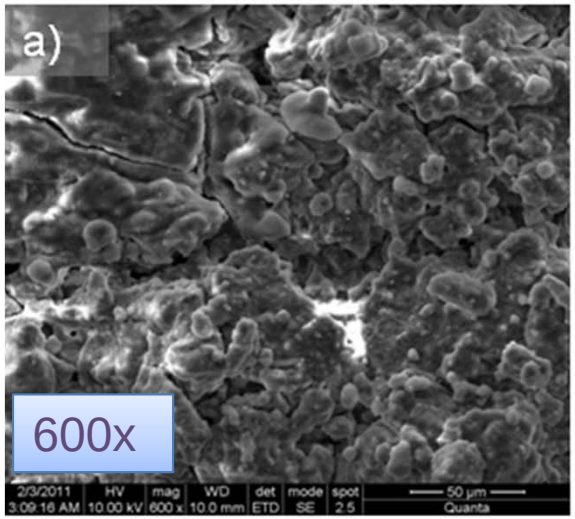


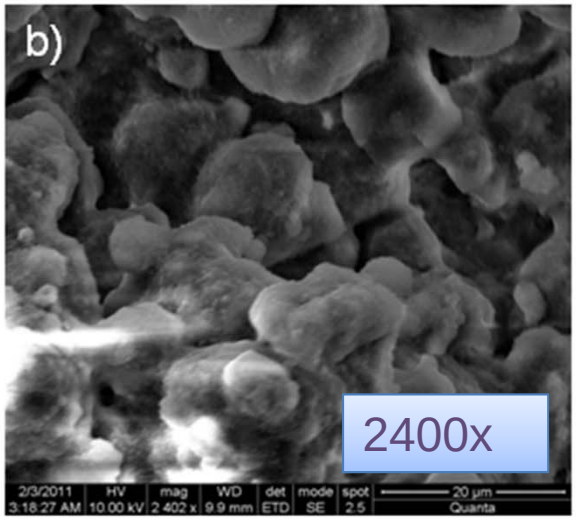
24000x

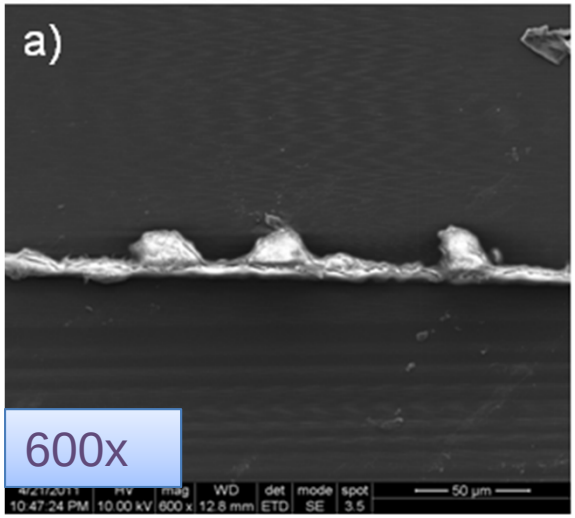
Aldrich Fumed 7 nm

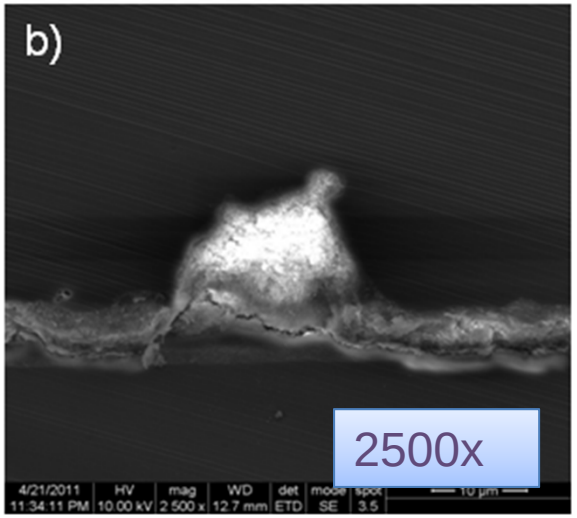
Hi-Sil morphology is more variable, with more large aggregates

Morphology of FF-Fumed Silica / Viton Nanocomposites







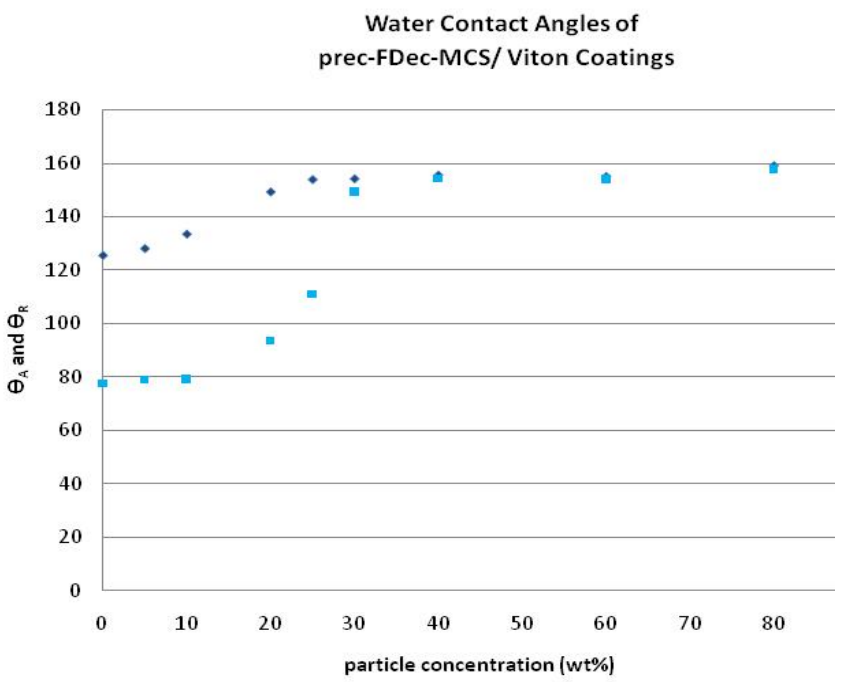


80 wt% FF-Fumed Silica in Viton®

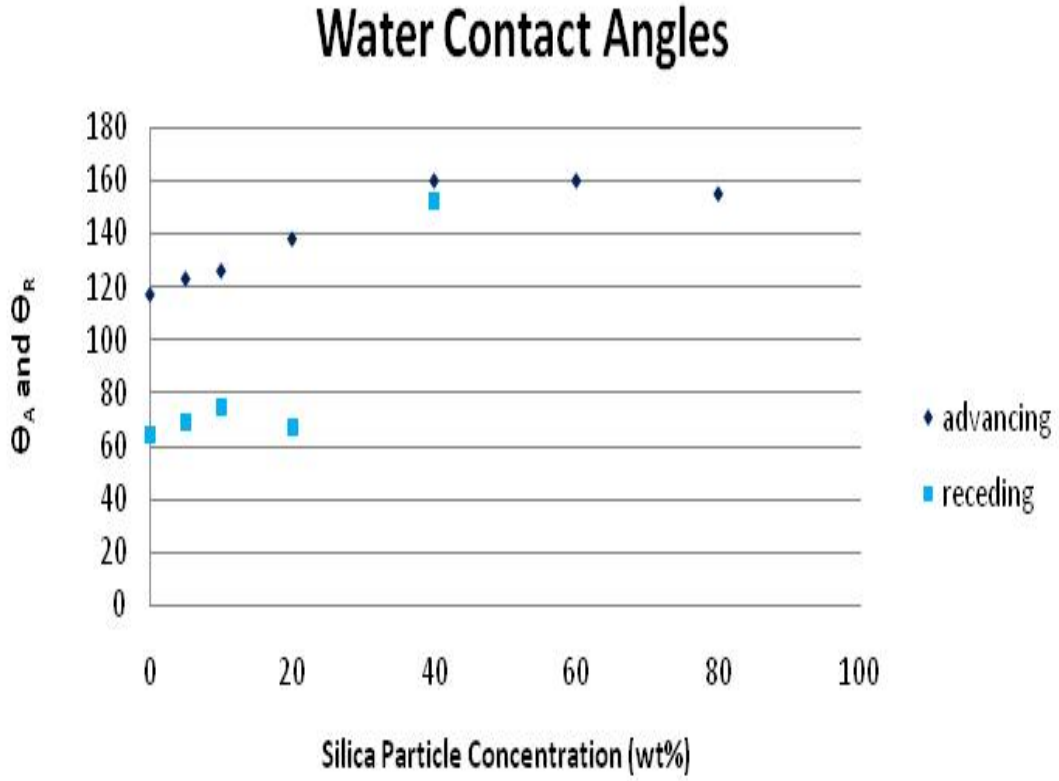
Smoother surface should limit fine sale roughness

Water Contact Angles for FF-Silica Nanocomposites

FF-HiSil233 in Viton®



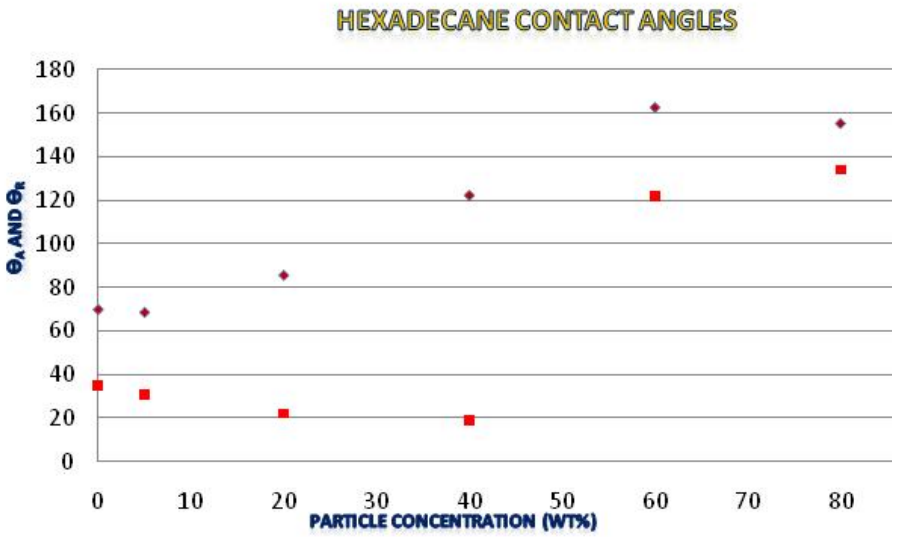
FF-HiSil233 in Technoflon®



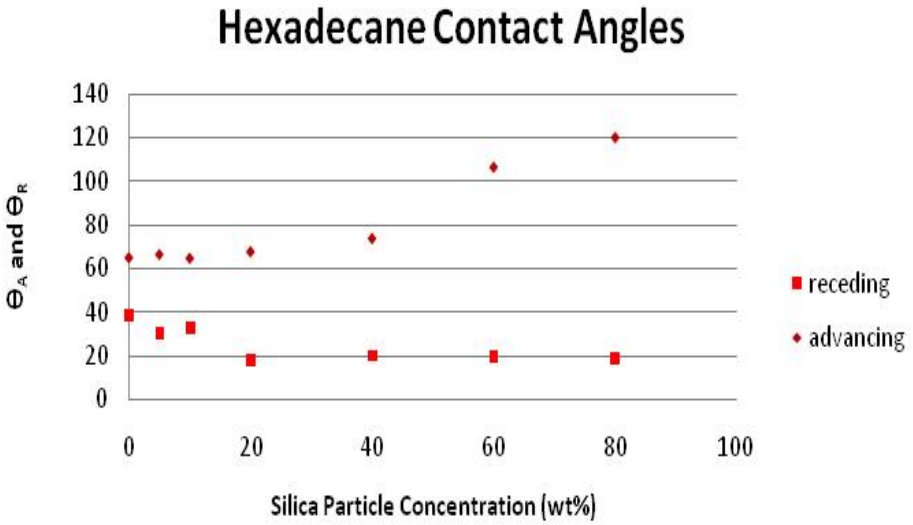
Similar water repellence for FF-Hi-Sil233 for different fluoropolymer types.
Somewhat lower receding angles for Technoflon® at low loading

Hexadecane Contact Angles for FF-Silica Nanocomposites

FF-HiSil233 in Viton®



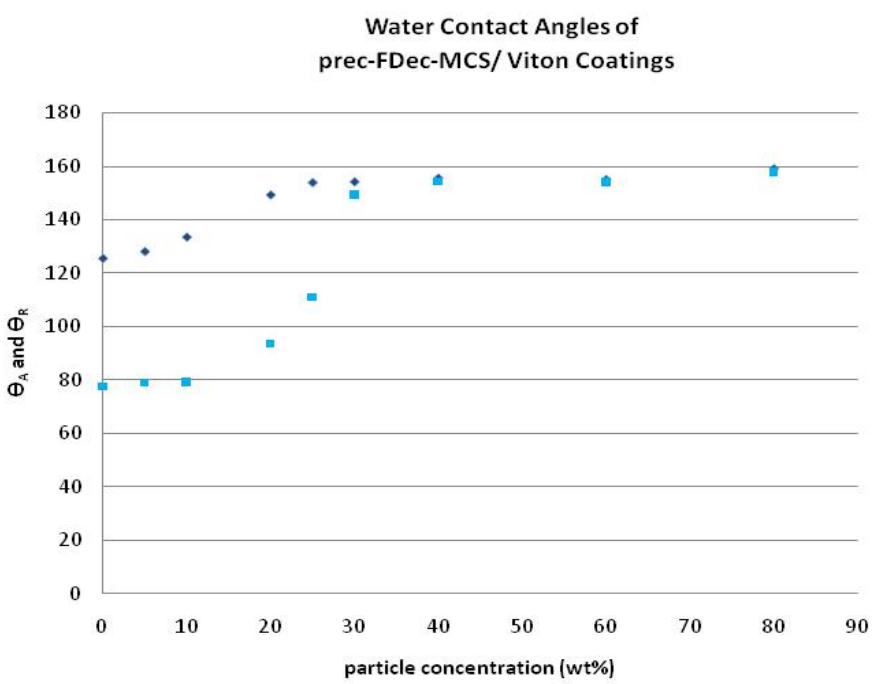
FF-HiSil233 in Technoflon®



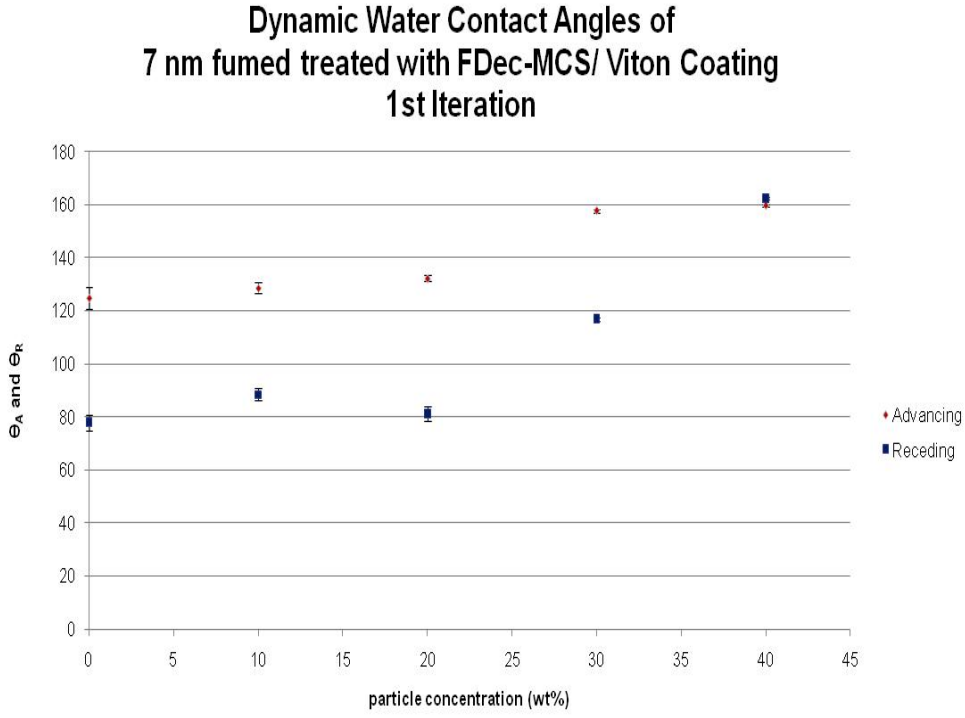
Despite similar contact angles at low loadings, systems incorporating Viton® achieve superoleophobic behavior, while those based on Technoflon® do not

Water Contact Angles for FF-Silica Nanocomposites

FF-HiSil233 in Viton®

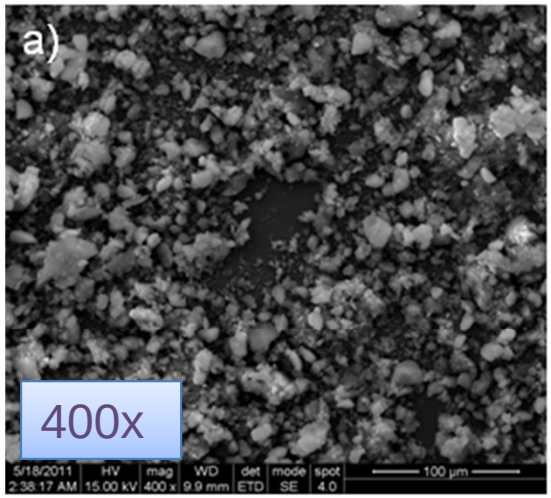


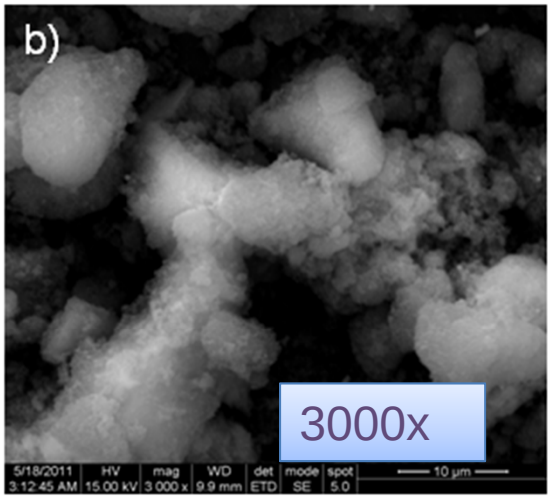
FF-Fumed Silica in Viton®



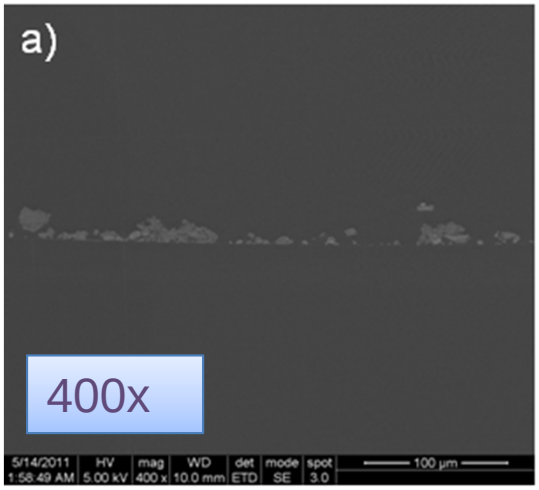
With fumed silica, the transition to superhydrophobic behavior requires a higher silica loading, likely due to the smoother nature of the silica aggregates

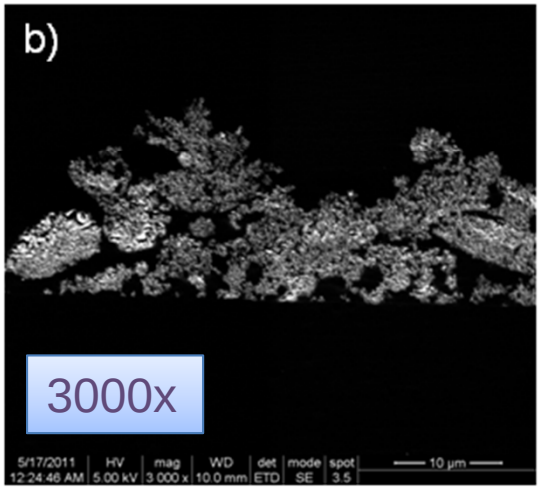
Morphology of Untreated Hi-Sil233 / Viton Nanocomposites

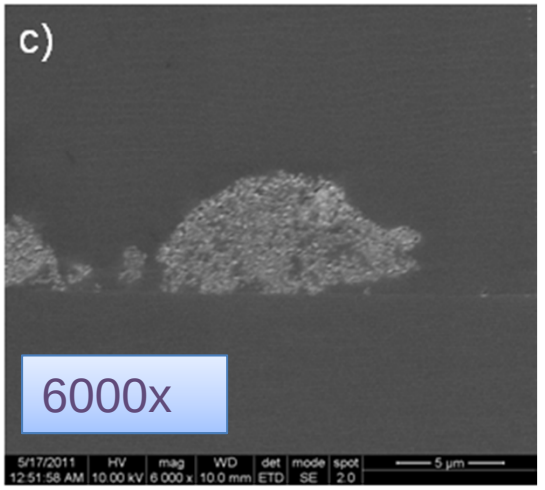




Hi-Sil233 Precipitated Silica, 80 wt% in Viton®, no treatment

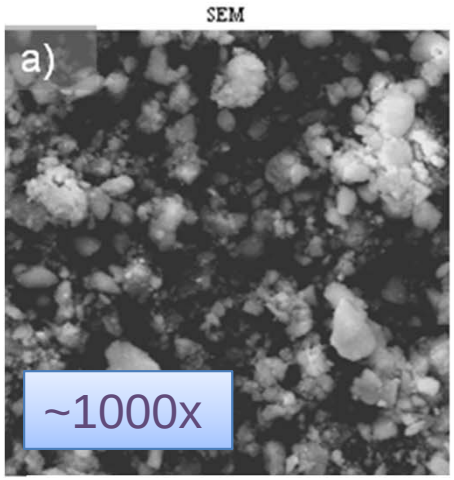


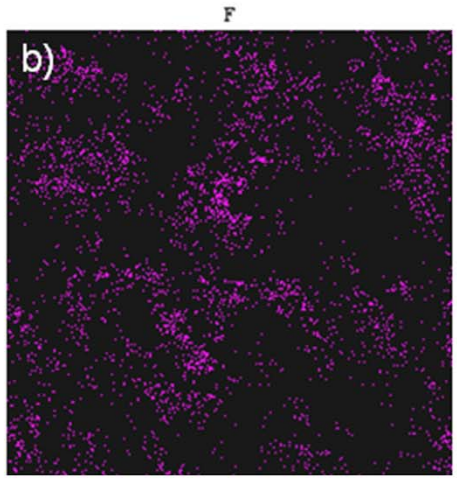


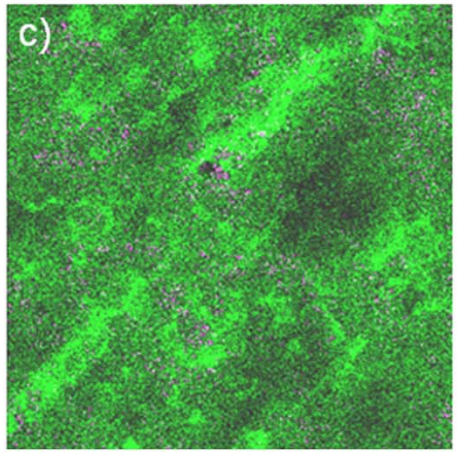


Smoother surface, leads to higher weight fractions needed for liquid repellence

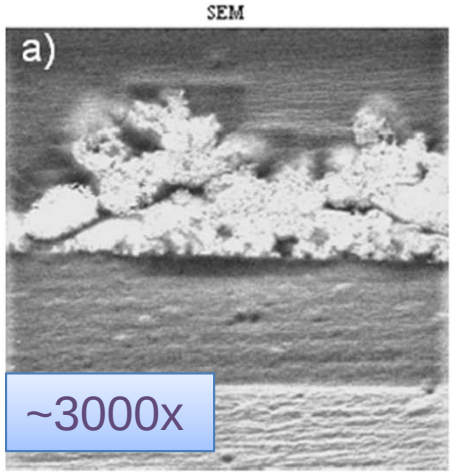
Morphology of Untreated Hi-Sil233 / Viton Nanocomposites

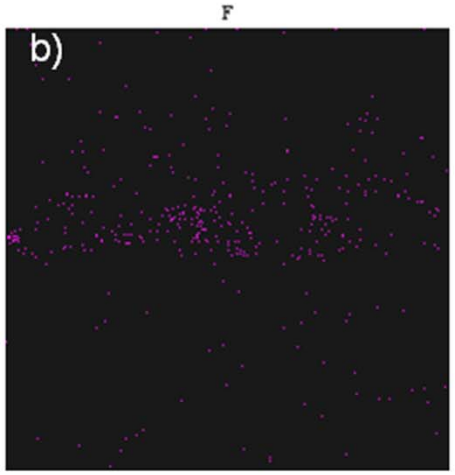


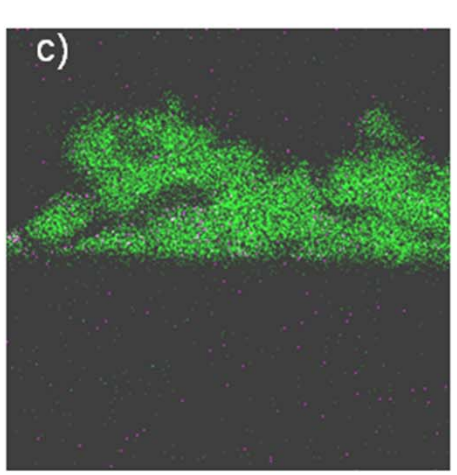




Hi-Sil233 Precipitated Silica, 80 wt% in Viton®, no treatment

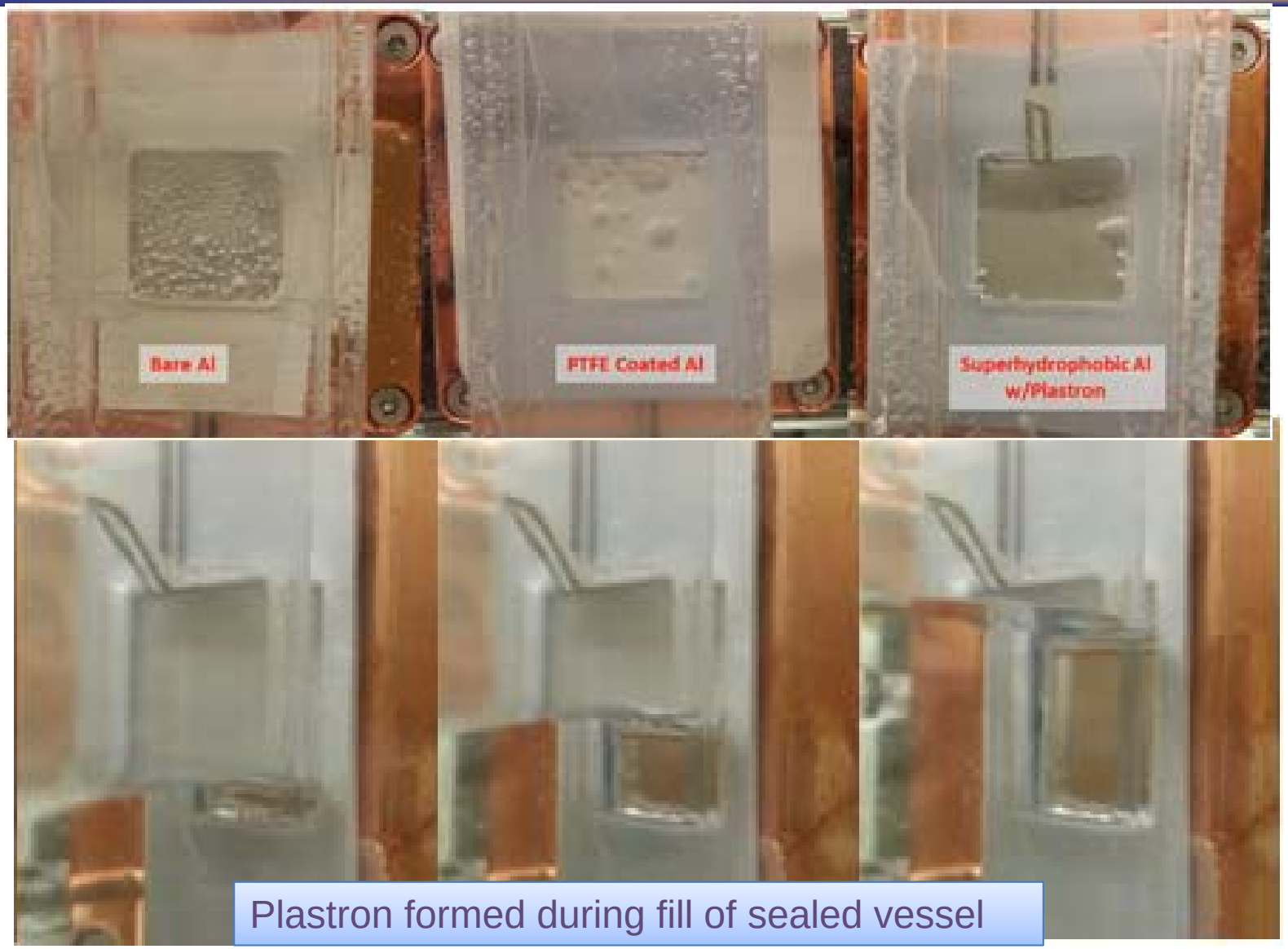






Fluorine tends to be evenly distributed among interstices of aggregate, enriched near bottom, but does not pool on the surface

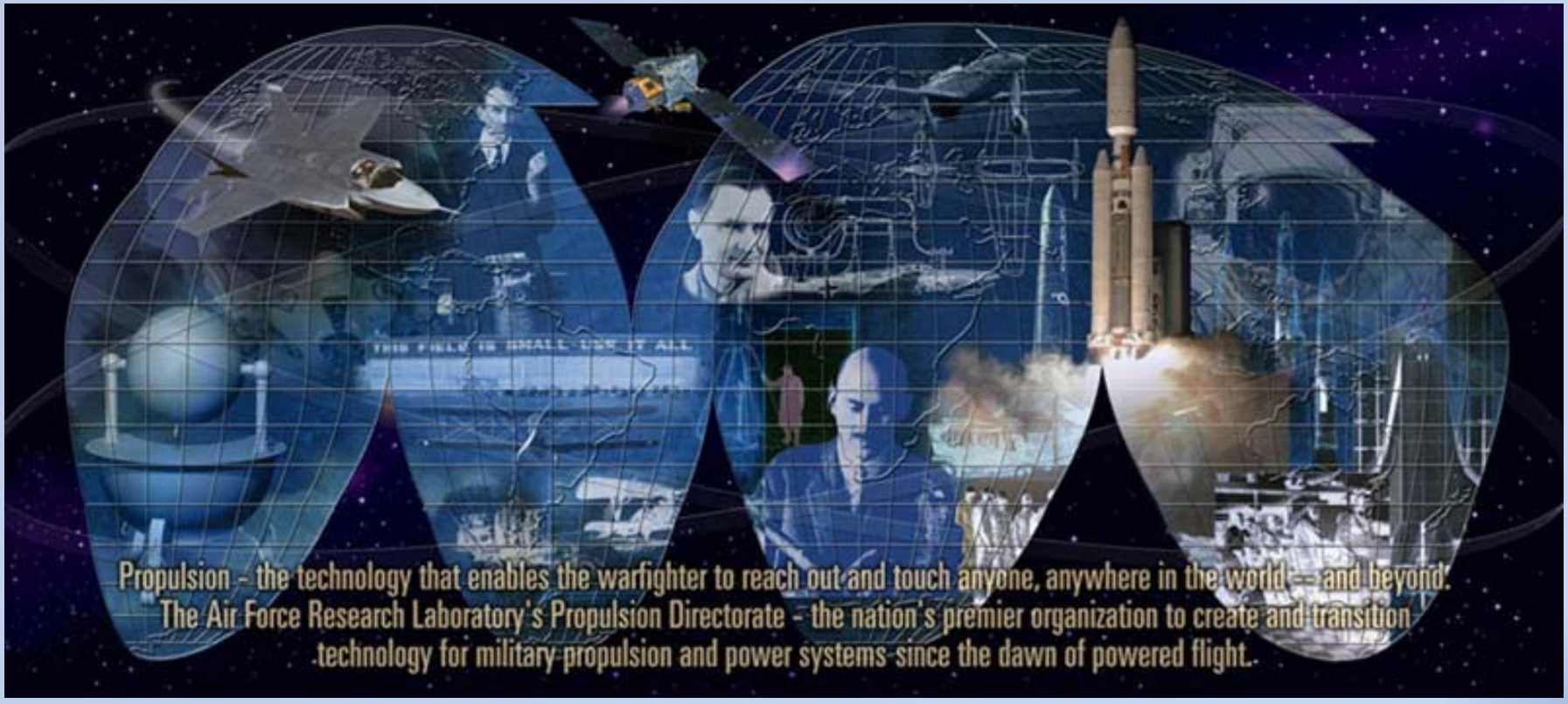
FF-Silica Nanocomposites Support Plastron Formation



Plastron formed during fill of sealed vessel

Summary

- Fluoroalkyl-functionalized silica particles and fluoropolymers can be spray coated on to a variety of substrates to form superamphiphobic surfaces
- The morphology of these silica / fluoropolymer sprayed surfaces is dominated by the roughness characteristics of the silica aggregates, and the degree to which the fluoropolymer creates a smoother surface topography
- In general, at low silica loadings, excess fluoropolymer eliminates roughness at the smallest length scales, decreasing the liquid repellence of the surface
- In experiments to date, precipitated silica, which tends to form aggregates with roughness across a wider range of length scales, has produced greater liquid repellence than fumed silica
- In untreated silica at the highest loadings, fluoropolymer does not appear to cover the surface evenly enough to produce a high level of liquid repellence



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